Synergistic Effects in the Epoxidation of Mixtures of Styrene and Aliphatic Alkenes catalysed by a Cytochrome P-450 Model

Alexander W. van der Made, Marc J. P. van Gerwen, Wiendelt Drenth, and Roeland J. M. Nolte

Department of Organic Chemistry, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

In competitive experiments styrene increases the rate of epoxidation of aliphatic alkenes by the mono-oxygenase model (*meso*-tetraphenylporphyrinato)manganese(III) chloride–sodium hypochlorite; this effect is caused by phenylacetaldehyde, which is formed as a side-product of styrene epoxidation.

Biomimetic oxidation by single oxygen donors catalysed by synthetic metalloporphyrins is an area of active research.[1—3] Recently, we reported on the mechanism of alkene epoxidation by the cytochrome P-450 model (*meso*-tetraphenylporphyrinato)manganese(III) chloride with sodium hypochlorite as oxidant (Meunier system[2a]).[3] In competitive experiments we observed that styrene increases the rate of epoxidation of aliphatic alkenes.[3c] We now present evidence that this rate enhancing effect is caused by aldehydes, which are formed as by-products in the epoxidation reaction.

Experiments were performed in a two phase water–dichloromethane system with triethylbenzylammonium chloride (TEBA) as phase transfer catalyst.† Rates were determined by measuring the formation of epoxide by g.l.c. Under the experimental conditions used, the order in alkene is 0. For aliphatic alkenes in non-competitive experiments the order in (*meso*-tetraphenylporphyrinato) Mn(III) chloride (MnTPP) varies between 1 and 0 (Figure 1).

In competitive experiments with styrene (molar ratio of aliphatic alkene to styrene 1 : 1) the epoxidation rate of the aliphatic alkene increases and the order in catalyst changes from less than one to first order. In order to trace the origin of this phenomenon we tested the effect of various additives. We found that phenylacetaldehyde, which is formed from styrene as a by-product (*ca.* 20%[1a,2d]), induces a similar change in kinetics. Other aldehydes (benzaldehyde, propionaldehyde, hexanal) also showed this behaviour, although the effects are less pronounced (Figure 1). Ketones, *e.g.* cyclohexanone and cyclopentanone, also accelerate the epoxidation reaction. Further experiments were performed using phenylacetaldehyde or benzaldehyde as additive. The following observations were made: (i) Without TEBA, no epoxidation takes place.The reaction cannot be induced by adding aldehyde, indicating that the aldehyde does not act as a phase transfer catalyst for OCl^-. (ii) Experiments performed with cyclohexene (0.626 mol dm^{-3}) to which various concentrations of benzaldehyde (0—0.623 mol dm^{-3}) were added, reveal that the epoxidation rate is first order in aldehyde (k_1 $4.2 \pm 0.1 \times 10^{-4}$ s^{-1}; Figure 1 inset). Substitution (4-NO_2, 4-F, 4-Me, 4-MeO) of the phenyl ring of benzaldehyde has virtually no influence on the rate of epoxidation of cyclohexene. (iii) The rate enhancing effect of the aldehyde depends on the steric environment of the porphyrin catalyst and decreases in the series MnTPP > (*meso*-tetramesityl-porphyrinato) Mn(III) chloride (MnTMP) > [*meso*-tetra(2,6-dichlorophenyl)porphyrinato] Mn(III) chloride (MnTDCP) (Table 1). (iv) The aldehyde is partly converted into carboxylic acid; for the combination benzaldehyde (0.156 mol dm^{-3}) and cyclohexene (0.626 mol dm^{-3}) the rates of benzoic acid formation and cyclohexene oxide formation are $1.62 \pm 0.05 \times 10^{-5}$ and $17.4 \pm 0.1 \times 10^{-5}$ mol dm^{-3} s^{-1}, respectively. In separate experiments we found that benzoic acid has no rate enhancing effect on the epoxidation of cyclohexene.

We explain these results as follows. In a rate determining step, manganese(III) porphyrin reacts with hypochlorite to form an oxomanganese(V) porphyrin complex (**1**).[3d] Without aldehyde, this complex has two decomposition routes: one with alkene to give an epoxide, equation (1), and a second one with manganese(III) to form an unreactive dimer, equation (2).

$$Mn^{V}{=}O + >C{=}C< \rightarrow Mn^{III} + >C(O)C< \quad (1)$$

(**1**)

$$Mn^{V}{=}O + Mn^{III} \rightleftarrows Mn^{IV}OMn^{IV} \quad (2)$$

As we have shown previously[3d] equation (2) is much more important for sterically unhindered porphyrins (MnTPP) than

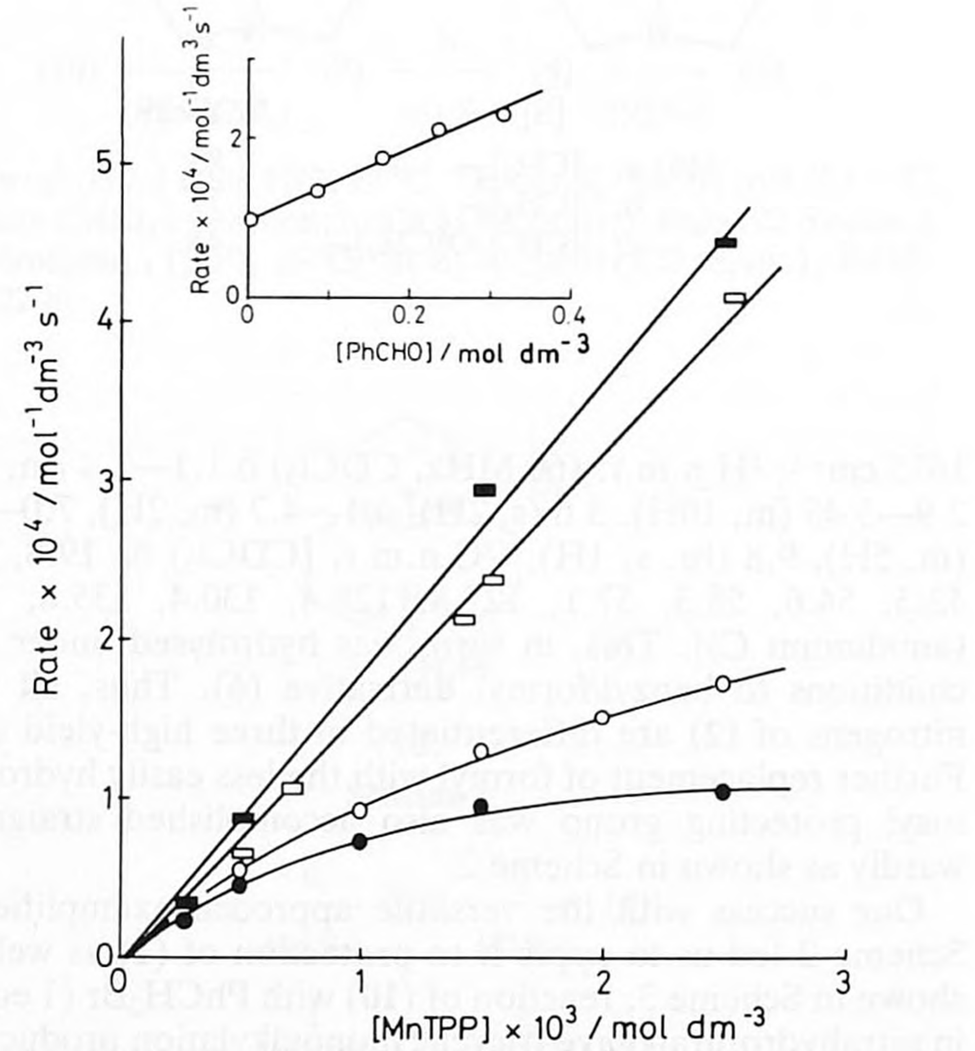
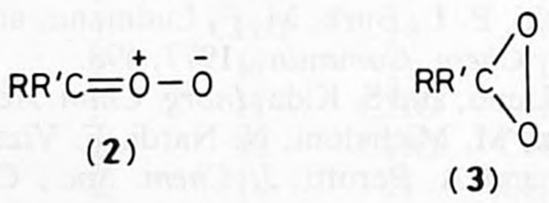


Figure 1. Rate of cyclohexene epoxidation as a function of [MnTPP] in the presence of styrene (0.313 M, □), phenylacetaldehyde (0.156 M, ■), benzaldehyde (0.156 M, ○), and without additive (●). Inset: rate of cyclohexene epoxidation as a function of [benzaldehyde]. For reaction conditions see footnote †.



(**2**) (**3**)

† Unless otherwise indicated the following reaction conditions were used: [MnTPP] 2.5×10^{-3}, [TEBA] 5×10^{-3}, [alkene] 0.626, [4-methylpyridine] 1.3 mol dm^{-3} in CH_2Cl_2 (volume organic phase 0.63 ml), aqueous NaOCl (2 ml, 0.35 mol dm^{-3}, pH 12.7). For experimental procedures see ref. 3b.

Table 1. Rate of cyclohexene epoxidation by manganese porphyrin catalysts in the presence and absence of phenylacetaldehyde.[a]

Catalyst	Rate × 10^5/mol dm^{-3} s^{-1} [b] with aldehyde	Rate × 10^5/mol dm^{-3} s^{-1} [b] without aldehyde	Ratio of rate constants
MnTPP	44.0	10.8	4.1
MnTMP	5.7	3.4	1.68
MnTDCP	1.53	1.33	1.15

[a] [$PhCH_2CHO$] 0.156 mol dm^{-3}. For reaction conditions, see footnote †. [b] Estimated error 5%.

for sterically hindered ones (MnTMP, MnTDCP). With aldehyde the oxygen atom transfer from (**1**) to a substrate is accelerated which causes less dimer to be formed. As a consequence, the epoxidation rate increases and the order in catalyst changes from less than one to first order. U.v.–visible measurements support this: without aldehyde the oxomanganese(v) species ($\lambda_{max.}$ 422 nm) decomposes with a rate constant k_1 3×10^{-4} s^{-1}. In the presence of 0.156 mol dm^{-3} of benzaldehyde the decomposition rate is accelerated to such an extent that we were unable to measure it ($k_1 \gg 3 \times 10^{-2}$ s^{-1}).

How aldehydes facilitate the oxygen transfer from oxomanganese(v) porphyrins to alkenes is not clear yet. Low temperature u.v.–visible experiments indicate that no intermediate complex is formed between (**1**) and aldehyde.[1b] The aldehyde could transfer a hydrogen atom to the oxygen atom of (**1**) to give a Mn(IV)OH porphyrin complex.[3c] We think that such a mechanism is unlikely as other hydrogen donating compounds (*e.g.* isopropylbenzene) were found to be unreactive in the epoxidation reaction. Also, the observation that ketones accelerate the epoxidation reaction does not favour a hydrogen transfer mechanism.

We tentatively propose that species (**1**) rapidly reacts with an aldehyde or a ketone to form a carbonyl oxide species (**2**) or a dioxirane (**3**). Compounds of type (**3**) are known to be effective epoxidizing agents.[4]

Recently a number of studies have appeared in which mechanistic conclusions are drawn from competitive experiments with styrene and aliphatic alkenes.[1h,2b,2c] In view of the results presented here, a re-evaluation of these experiments may be required.

Received, 6th January 1987; Com. 020

References

1 (a) J. T. Groves and T. E. Nemo, J. *Am. Chem. Soc.,* 1983, **105**, 5786; (b) J. T. Groves and Y. Watanabe, *ibid.,* 1986, **108**, 507; (c) T. G. Traylor, T. Nakano, B. E. Dunlap, P. S. Traylor, and D. Dolphin, *ibid.,* 1986, 2782; (d) C. M. Dicken, F. L. Fu, M. W. Nee, and T. C. Bruice, *ibid.,* 1985, **107**, 5776; (e) J. A. Smegal and C. L. Hill, *ibid.,* 1983, **105**, 3515; (f) J. R. Lindsay Smith, M. W. Nee, J. B. Noar, and T. C. Bruice, *J. Chem. Soc., Perkin Trans. 2,* 1984, 255; (g) J. P. Renaud, P. Battioni, J. F. Bartoli, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1985, 888; (h) K. Srinivasan, P. Michaud, and J. K. Kochi, *J. Am. Chem. Soc.,* 1986, **108**, 2309.

2 (a) B. Meunier, E. Guilmet, M. De Carvalho, and M. E. Poilblanc, *J. Am. Chem. Soc.,* 1984, **106**, 6668; (b) J. P. Collman, J. I. Brauman, B. Meunier, T. Hayashi, T. Kodadek, and S. A. Raybuck, *ibid.,* 1985, **107**, 2000; (c) J. P. Collman, T. Kodadek, S. A. Raybuck, J. I. Brauman, and L. M. Papazian, *ibid.,* 1985, **107**, 4343; (d) J. P. Collman, T. Kodadek, and J. I. Brauman, *ibid.,* 1986, **108**, 2588.

3 (a) J. A. S. J. Razenberg, R. J. M. Nolte, and W. Drenth, *Tetrahedron Lett.,* 1984, **25**, 789; (b) J. A. S. J. Razenberg, A. W. van der Made, J. W. H. Smeets, and R. J. M. Nolte, *J. Mol. Catal.,* 1985, **31**, 271; (c) J. A. S. J. Razenberg, R. J. M. Nolte, and W. Drenth, *J. Chem. Soc., Chem. Commun.,* 1986, 277; (d) R. J. M. Nolte, J. A. S. J. Razenberg, and R. Schuurman, *J. Am. Chem. Soc.,* 1986, **108**, 2751.

4 G. Cicala, G. R. Curci, M. Fiorentino, and O. Laricchiuta, *J. Org. Chem.,* 1982, **47**, 2670; R. W. Murray and R. Yeyamaran, *ibid.*, 1985, **50**, 2847.

A Pentuply-bridging Carbonyl Group: Crystal and Molecular Structure of a Salt of the 1-Oxo-2-phenyl-1,2-dicarbadodecaborate(12) Anion, $[LH]^+[O(Ph)C_2B_{10}H_{10}]^-$ (L = 1,8-*N,N,N′,N′*-tetramethylnaphthalenediamine)

David A. Brown,[a] William Clegg,[b] Howard M. Colquhoun,[c] J. Anthony Daniels,[c] Ian R. Stephenson,[a] and Kenneth Wade*[a]

[a] *Department of Chemistry, Durham University Science Laboratories, South Road, Durham DH1 3LE, U.K.*
[b] *Department of Inorganic Chemistry, The University, Newcastle-upon-Tyne NE1 7RU, U.K.*
[c] *ICI Chemicals and Polymers Group, The Heath, Runcorn, Cheshire WA7 4QE, U.K.*

Deprotonation of the C-hydroxy *ortho*-carborane 1,2-$HO(Ph)C_2B_{10}H_{10}$ by 1,8-*N,N,N′,N′*-tetramethylnaphthalenediamine gives a salt whose anion, $[O(Ph)C_2B_{10}H_{10}]^-$, effectively consists of a *nido*-shaped $[PhCB_{10}H_{10}]^-$ residue capped by a pentuply-bridging carbonyl group whose C–O distance of 1.245(3) Å and position over the open carborane face, 2.001(3) Å from the cage carbon atom, are readily rationalized by frontier orbital considerations.

Although the derivative chemistry of icosahedral carboranes $C_2B_{10}H_{12}$ is now extensive,[1–3] C-hydroxy species $HO(R)C_2B_{10}H_{10}$ (**1**) have received surprisingly little attention, and none has been structurally characterised. In one of the few reported studies of such compounds,[4] it was noted that they are acidic, though the potential interest of the anions $[O(R)C_2B_{10}H_{10}]^-$ (**2**) generated on deprotonation of (**1**) went unremarked. The delocalization of anionic charge into the carborane cage expected in (**2**) allows such anions to be regarded as *nido*-shaped residues $[RCB_{10}H_{10}]^-$ stabilised by pentuply-bridging carbonyl groups (**3**), an environment consistent with the cluster-forming potential of CO units as